Status and Trends of Legacy and Emerging Contaminants Identified through the Great Lakes Fish Monitoring and Surveillance Program

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History

- The Great Lakes Fish Monitoring Program started in the late 1970s
- Partnership with Great Lakes States and Tribes and other Federal Agencies
- Complimentary EC program
- Last peer reviewed in 2007 (next in 2012 or 2013 jointly with EC)
- Data used by other agencies, Great Lakes states and Tribes, NGOs and other researchers

Great Lakes Fish Monitoring Program Pre-2010

Open Lake Trends Monitoring

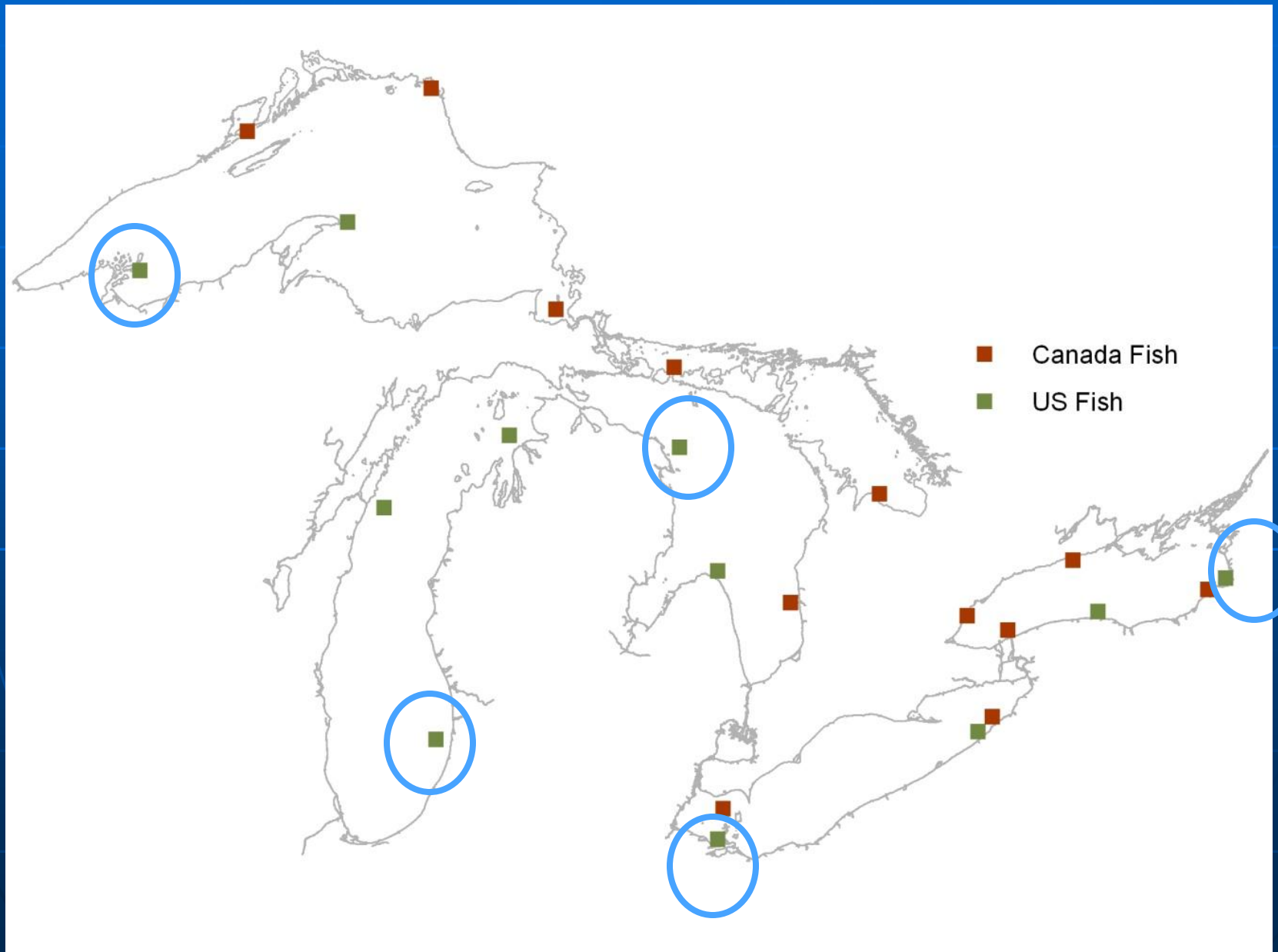
- Monitor contaminant trends in the open waters of the Great Lakes (using fish as indicators)
- Assess the overall effects of toxics on fish and fish-consuming wildlife
- Whole lake trout and walleye

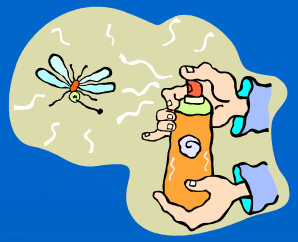
Sport Fish Fillet Program

Discontinued in 2008

- Monitor potential human exposure to contaminants through consumption of popular sport species
- Chinook and Coho salmon fillets

GLFMSP Collection Locations





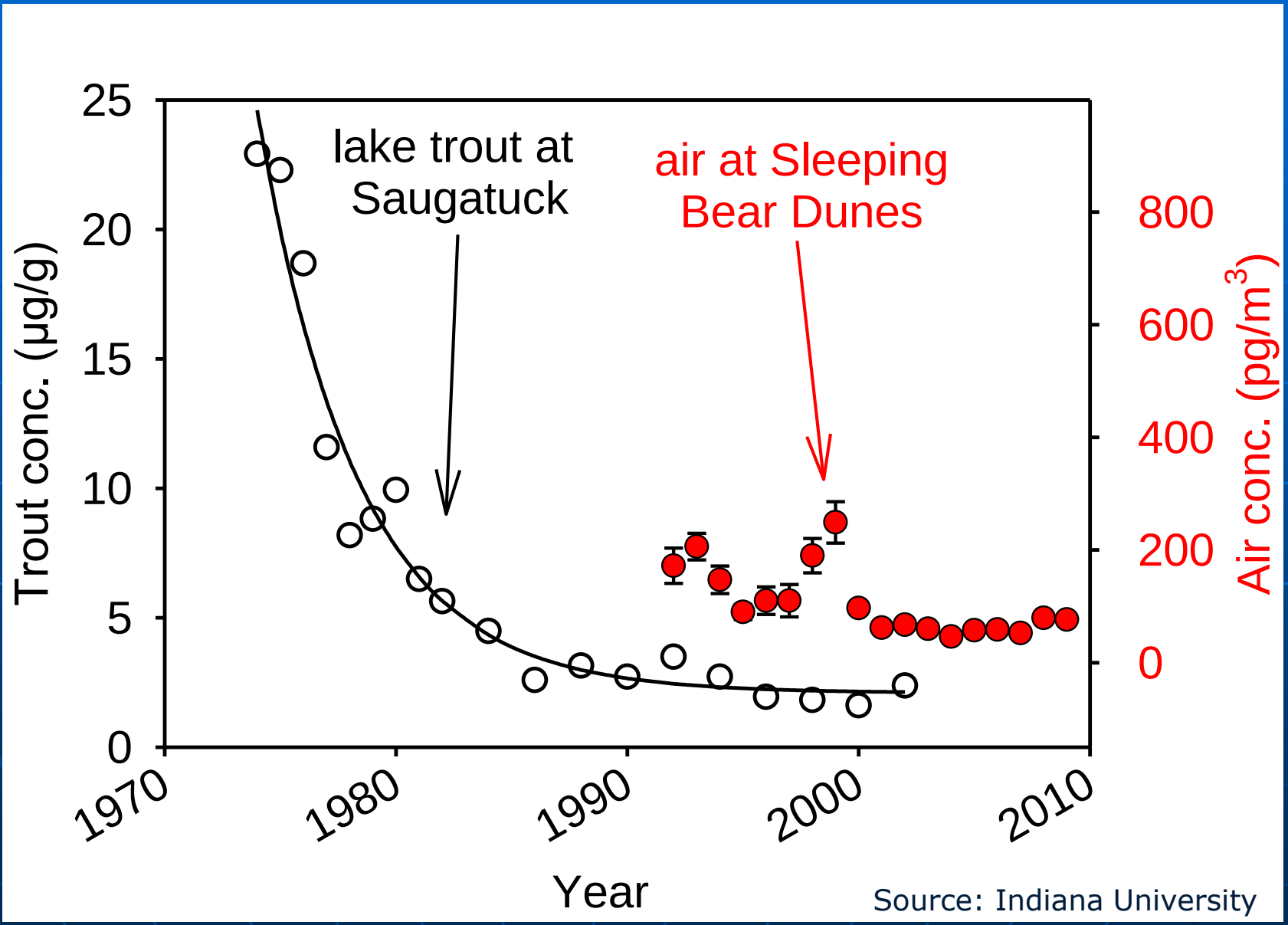
Legacy Contaminant List

- Legacy Contaminants

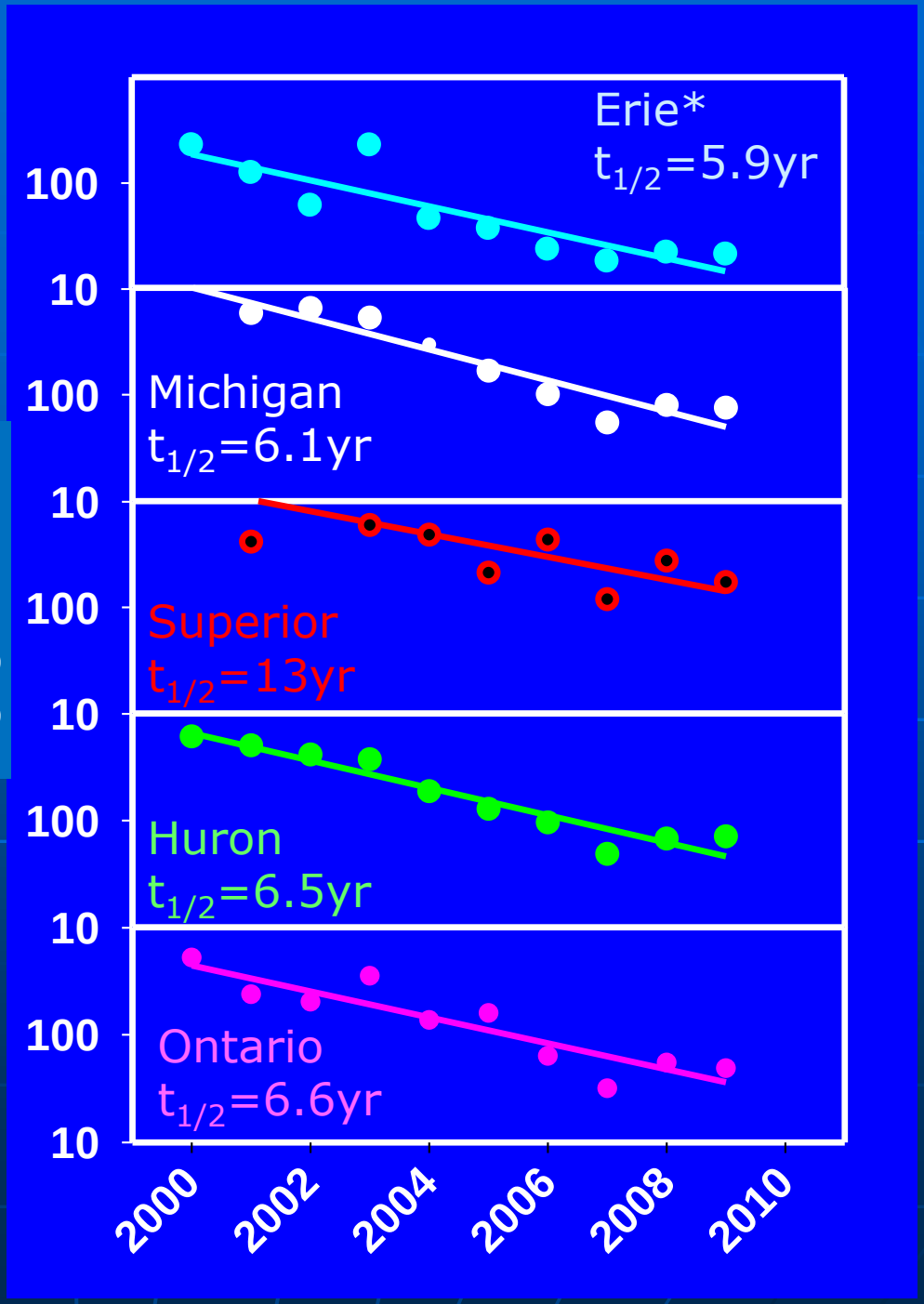
- PCB congeners
- PCB co-planers
- Hexachlorobenzene
- Octachlorostyrene
- Lindane
- Alpha BHC
- Dieldrin
- Heptachlor epoxide-b
- Cis-chlordane
- Trans- chlordane
- Oxychlordane
- Cis-nonachlor
- Trans- nonachlor

- pp,-DDT
- pp,-DDE
- pp,-DDD
- Endrin
- Mirex (Lake Ontario Only)
- Toxaphene& homologs

PCBs in Lake Michigan trout and air



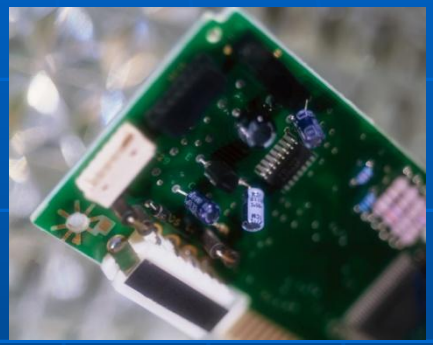
Whole Lake Trout Total Toxaphene Concentrations



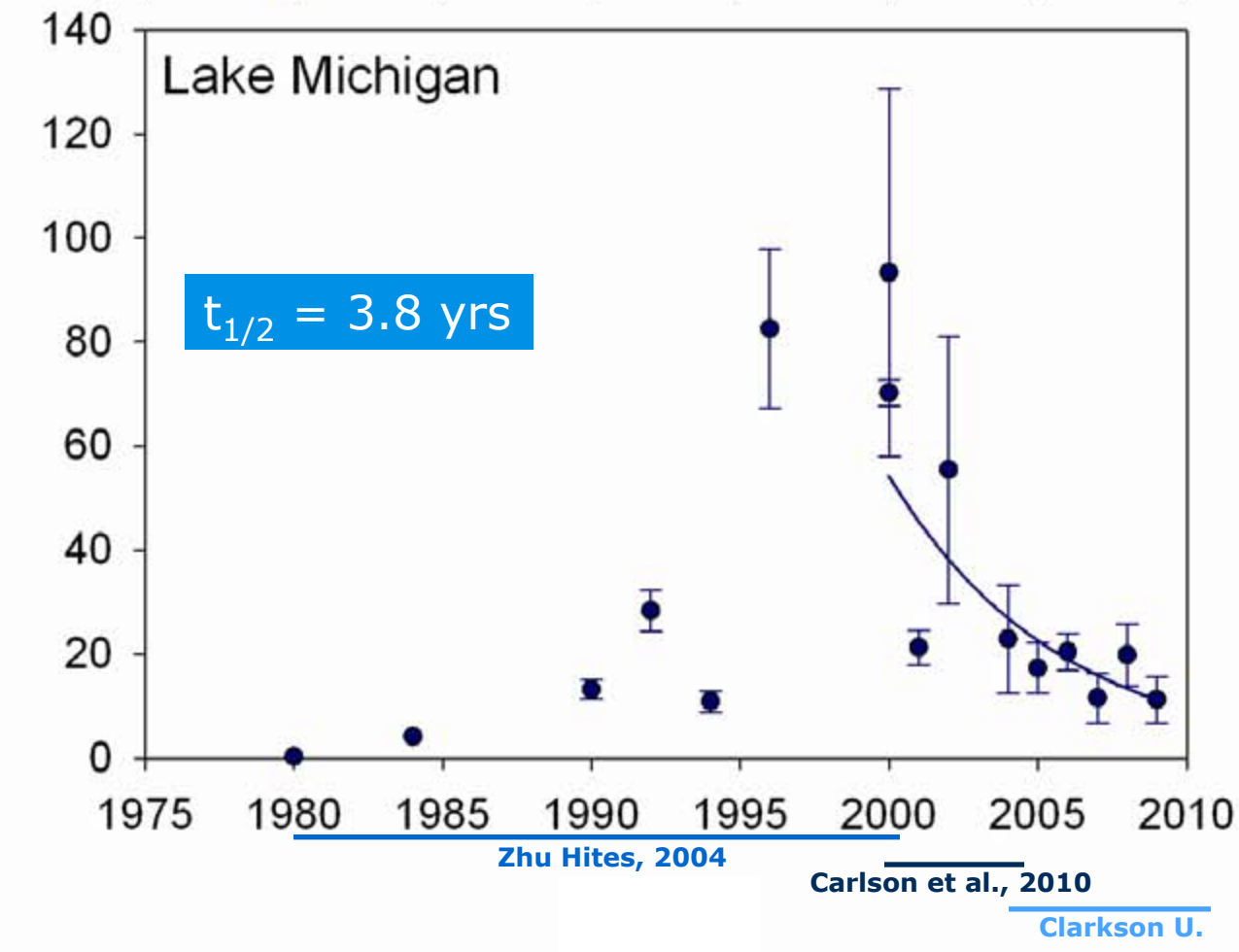
* Walleye

Current Use Contaminants List

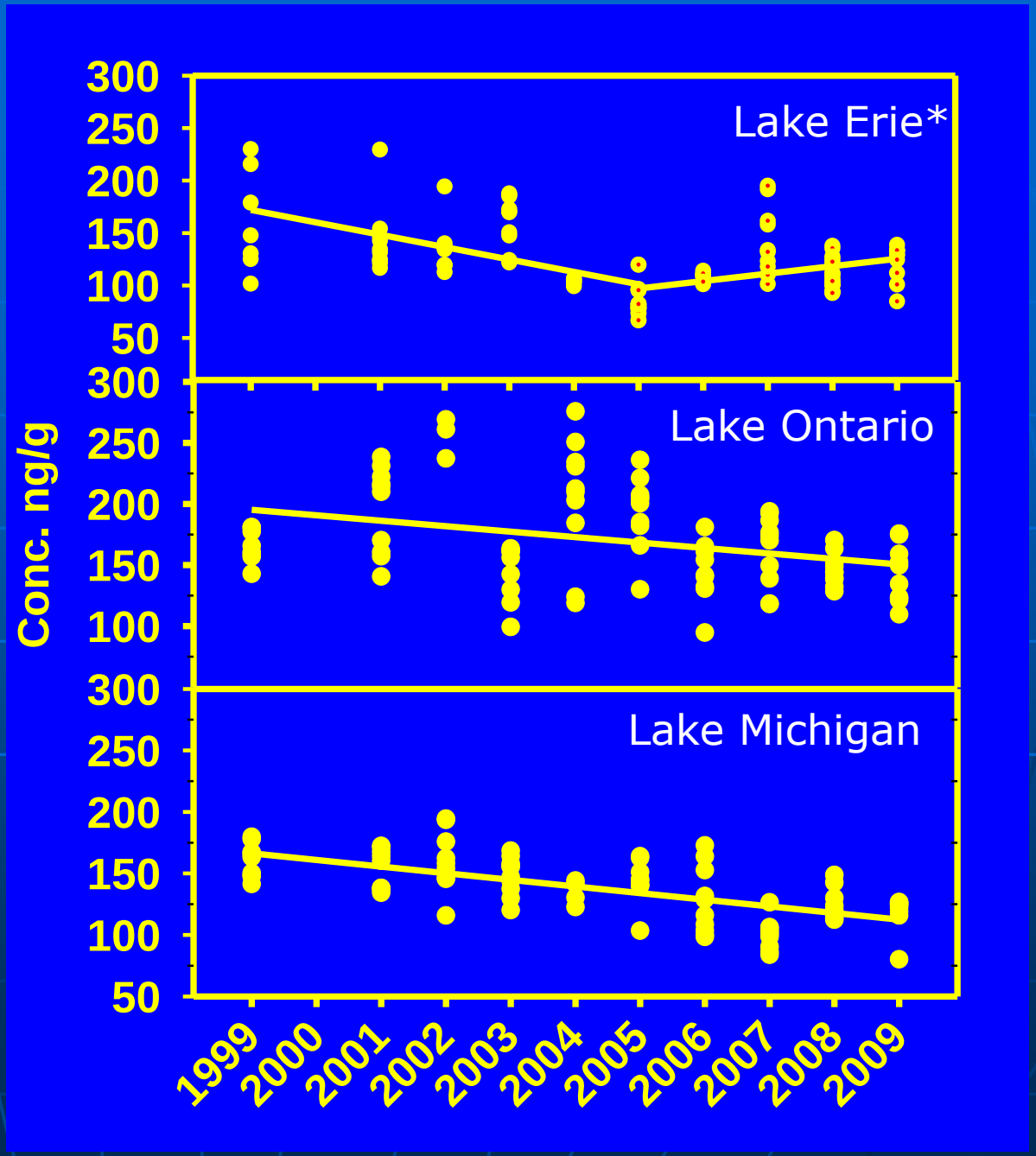
- PBDEs
- Hg
- PCDD/Fs



Mean Penta BDE Concentrations in Lake Michigan Whole Lake Trout (1980 – 2009)



Whole Lake Trout Total Hg Concentrations



* Walleye

Pushing the Science

1. Lake of the Year (LOY) intensive, take advantage of CSMI program resources

2. Comprehensive and quantitative screening for emerged and emerging contaminants of concern (EOCs) in lake trout

Lake of the Year (LOY) Program

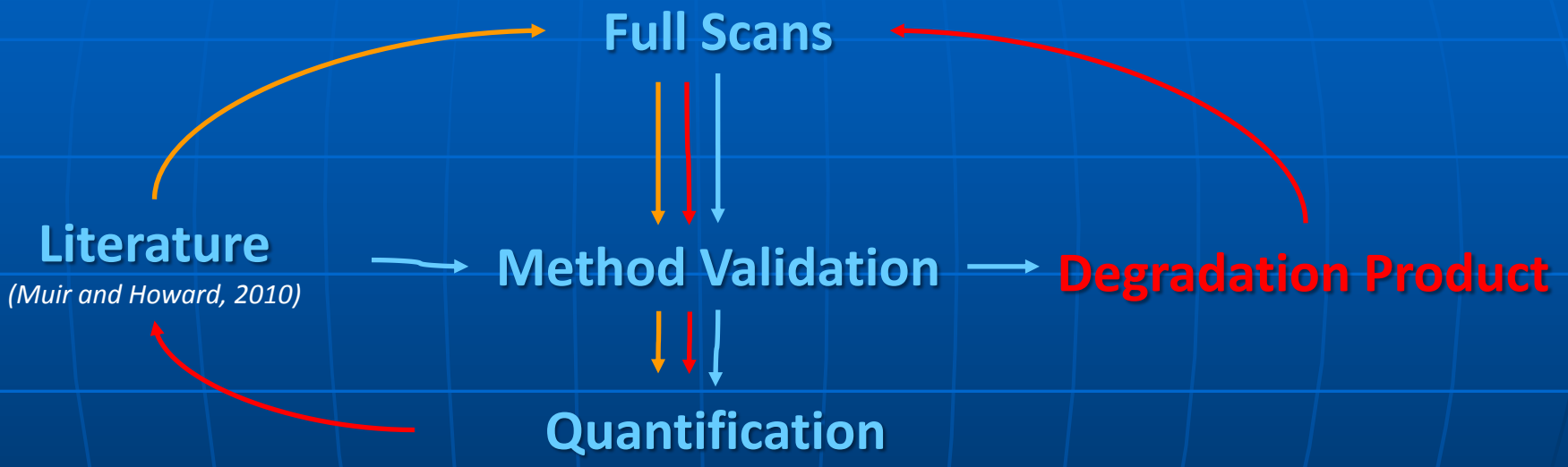
Top to bottom lake snapshot

Perform a detailed bioaccumulation study

- Water (dissolved and particulate)
- Phytoplankton
- Zooplankton
- Mussels
- Benthic macro invertebrates
- Forage fish
- Lake trout

Started with Lake Superior in the summer of 2011

Comprehensive and Quantitative Screening for Emerged and Emerging Contaminants of Concern

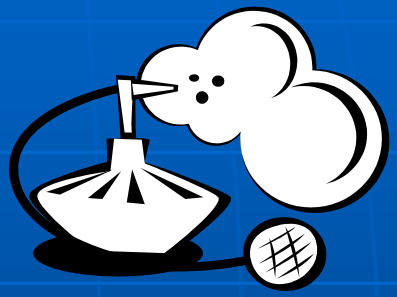


Mixed Method interplay for emerging contaminant discovery

Pushing the Science

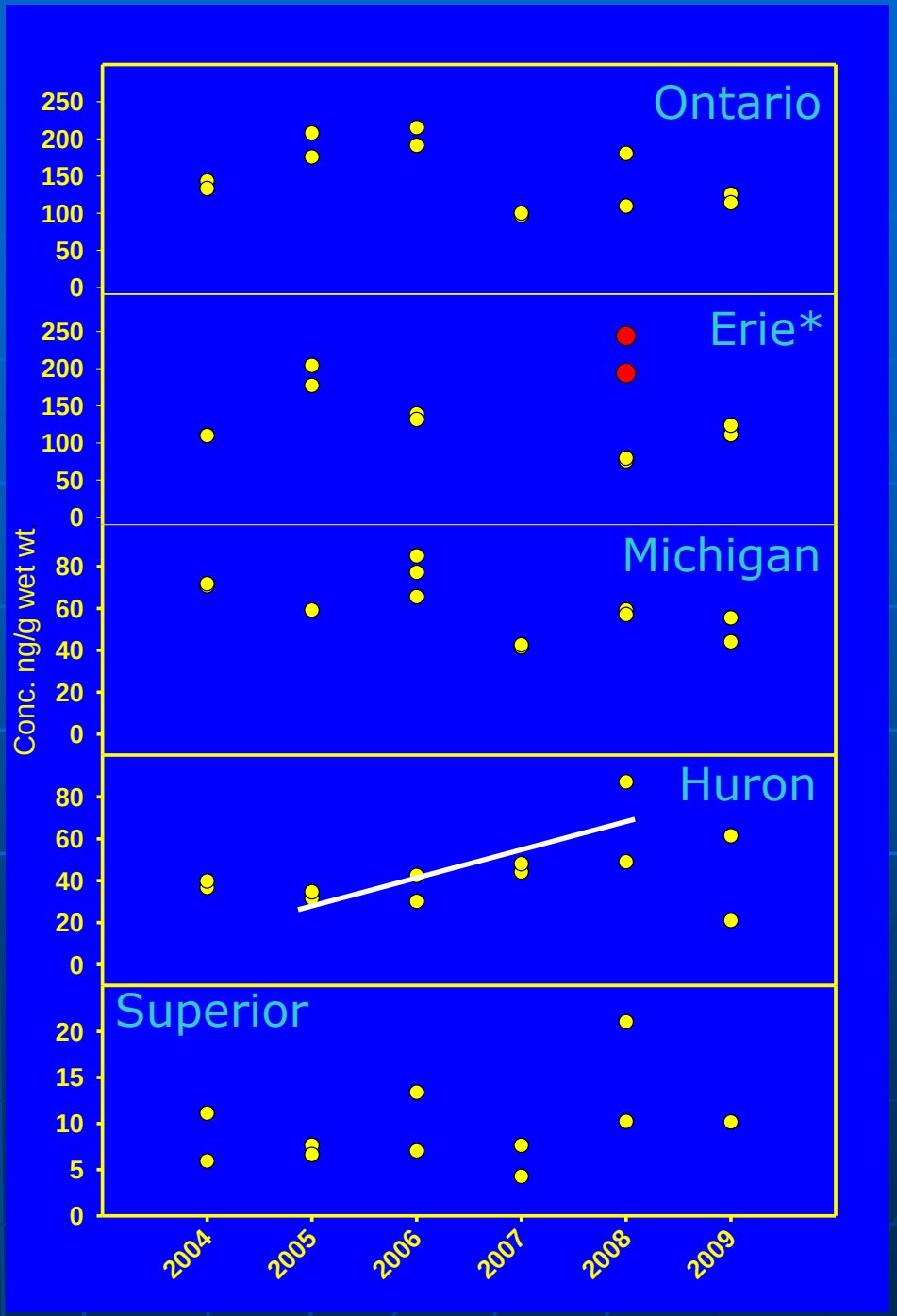
Literature Guided Search

PFOA, PFOS*
Fluorotelomer alcohols
Polychlorinated naphthalenes
Dacthal
Synthetic musks
Alkylphenols
Non-PBDE BFRs
Polybrominated biphenyls
Pharmaceuticals
Siloxanes
Trace metals including thallium



* Also measured in routine samples

Whole Fish PFOS Concentrations (2004-2009)



*Walleye, Trout

Collaboration and Cross-Pollination

1. Sediment collection/analysis (U of IL at Chicago) for complete top to bottom contaminant measurements.

2. Intercalibration of analytical methods with other programs and laboratories using split samples to provide a more robust dataset.

3. Collaboration with several states to help with technology transfer.

Outcomes, Expected Results and Collaboration Potential

Overreaching goals:

1. Provide a comprehensive evaluation of contaminant burdens in Great Lakes fish.

2. Using multi-component techniques, provide the most accurate and complete evaluation of emerging contaminant trophic transfer, biological influences (i.e. diet) and spatial distribution in the Great Lakes Basin.

3. Establish an analytical hub for emerging contaminant exploration, method development and validation.

4. Create a living dataset, searchable for years to come.

EPA's Great Lakes Human Health Fish Tissue Study

Leanne Stahl[1], John Wathen[1], Elizabeth Murphy[2], Jacqueline Fisher[2], Edwin Smith[2], Anthony Olsen[3], Blaine Snyder[4], and Harry McCarty[5]

Background

EPA's National Coastal Condition Assessment (NCCA) is a one of a series of probability-based surveys designed to assess the condition of U.S. waters. It includes collection and analysis of physical, chemical, and biological indicator data that will allow a statistically-valid characterization of the condition of the Nation's coastal waters. EPA developed an unequal probability design to select 682 marine sampling locations along the coasts of the United States and 225 freshwater sites from nearshore areas throughout the Great Lakes. The Office of Water (OW) is leading planning and implementation of the NCCA.

EPA is conducting fish contamination studies under the NCCA. One of these studies is the Great Lakes Human Health Fish Tissue Study. The Office of Science and Technology (OST) within OW, the Great Lakes National Program Office (GLNPO), and the Office of Research and Development (ORD) are combining resources and expertise to conduct this study. State and contractor-led field teams collected fish samples from a representative subset of 157 of the 225 nearshore sites in the Great Lakes during 2010. Preparation and analysis of fillet samples is currently underway. This is the first statistically-based assessment of a variety of chemicals in Great Lakes fish for human health applications.

Study Design

Assessment of chemicals in Great Lakes fish for human health applications involves:

- Sampling 157 randomly selected sites (about 30 sites per lake) in the nearshore region (depths up to 30 m or distances up to 5 km from shore) during 2010
- Collecting one fish composite sample from each site (optimally, 5 similarly-sized adult fish of the same species that are consumed by humans)
- Shipping samples to Microbac Laboratories in Baltimore, MD, for sample storage and preparation of fillet composite samples for analysis
- Analyzing the fillet samples for mercury, 13 perfluorinated compounds (PFCs), 5 fatty acids, 8 polybrominated diphenyl ether (PBDE) congeners, and up to 30 pharmaceutical compounds

Great Lakes Human Health Fish Tissue Study

- First statistically-based assessment of chemicals in Great Lakes fish related to human health
- 157 randomly selected sampling locations

Collaborators

OW/Office of Science and Technology
- Project Management
- Fish collection and tissue sample preparation
- Data validation and reporting

Great Lakes National Program Office
- Technical and fiscal support for fish sample collection and analysis

ORD/National Health and Environmental Effects Research Laboratory
- Study design development
- Sample tracking
- Statistical analysis of tissue data

Target Chemicals

Mercury
- Total mercury

Perfluorinated Compounds (PFCs)
- 13, including PFOA and PFOs

Fatty Acids
- 5, including ALA, EPA, and DHA

Polybrominated diphenyl ethers (PBDEs)
- 8 congeners

Pharmaceuticals
- 20–30 compounds

Sample Analysis

Fish Fillet Samples

Mercury
- TestAmerica Laboratories, Knoxville, TN

PFCs
- TestAmerica Laboratories, West Sacramento, CA

Fatty Acids
- Southwest Research Institute, San Antonio, TX

PBDEs and Pharmaceuticals
- To be determined

Target Chemicals

Metals

Common Name	CAS Number
Mercury (total)	7439-97-6

Perfluorinated Compounds

Common Name	Abbreviation	Formula	CAS Number
Perfluorobutyric acid	PFBA	C_3F_7COOH	375-22-4
Perfluoropentanoic acid	PFPeA	C_4F_9COOH	2706-90-3
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$	307-24-4
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$	375-85-9
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$	335-67-1
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$	375-95-1
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$	375-76-2
Perfluoroundecanoic acid	PFUnA	$C_{10}F_{21}COOH$	2058-94-8
Perfluorododecanoic acid	PFDoA	$C_{11}F_{23}COOH$	307-55-1
Perfluorobutanesulfonic acid	PFBS	$C_4F_9SO_3H$	375-73-5
Perfluorohexanesulfonic acid	PFHxS	$C_6F_{13}SO_3H$	355-46-4
Perfluorooctanesulfonic acid	PFOS	$C_8F_{17}SO_3H$	1763-23-1
Perfluorooctanesulfonamide	PFOSA	$C_8F_{17}SO_2NH_2$	754-91-6

Omega-3 Fatty Acids

Common Name	Abbreviation	Chemical Name	CAS Number
alpha-Linolenic acid	ALA	cis-9,12,15-octadecatrienoic acid	463-40-1
Eicosatrienoic acid	ETE	cis-11,14,17-eicosatrienoic acid	17046-59-2
Eicosapentaenoic acid	EPA	cis-5,8,11,14,17-eicosapentaenoic acid	10417-94-4
Docosapentaenoic acid	DPA	cis-7,10,13,16,19-docosapentaenoic acid	24880-45-3
Docosahexaenoic acid	DHA	cis-4,7,10,13,16,19-docosahexaenoic acid	6217-54-5

Polybrominated Diphenyl Ethers

Chemical Name	Congener	CAS Number
2,2',4,4'-Tetrabromodiphenyl ether	47	5436-43-1
2,3',4,4'-Tetrabromodiphenyl ether	66	189084-61-5
2,2',4,4',5-Pentabromodiphenyl ether	99	60348-60-9
2,2',4,4',6-Pentabromodiphenyl ether	100	189084-64-8
2,2',3,4,4',5'-Hexabromodiphenyl ether	138	182677-30-1
2,2',4,4',5,5'-Hexabromodiphenyl ether	153	68631-49-2
2,2',4,4',5,6'-Hexabromodiphenyl ether	154	207122-15-4
2,2',3,4,4',5',6-Heptabromodiphenyl ether	183	207122-16-5

Pharmaceutical Compounds

Common Name	CAS Number
20–30 Pharmaceuticals (TBD)	TBD

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For more information visit: ***http://water.epa.gov/scitech/swguidance/fishstudies/index.cfm***

GLFMSP Publications

In Preparation

Chang, F., Xia, X., Hopke, P.K., Crimmins, B.S., Pagano, J.J., Milligan, M.S., Holsen, T.M., To be submitted to Environmental Science and Technology, PCB trends in Great Lake Predator Fish.

In Review

Crimmins, B.S., Pagano, J.J., Xia, X., Hopke, P.K., Milligan, M.S., Holsen, T.M. In review, Environmental Science and Technology. Polybrominated diphenyl ethers (PBDEs) in Great Lakes lake trout: Turning the corner on PBDEs in the Great Lakes 1982 -2008.

Xia, X., Hopke, P.K., Crimmins, B.S., Pagano, J.J., Milligan, M.S., Holsen, T.M., In Review, Journal of Great Lakes Research. Toxaphene trends in the Great Lakes fish.

In Press

Zananski, T.J., Holsen, T.M., Hopke, P.K., Crimmins, B.S. In press, Ecotoxicology. Mercury temporal trends in top predator fish of the Laurentian Great Lakes.

Xia, X., Hopke, P.K. , Holsen, T.M., and Crimmins, B.S. **2011**. Modeling Toxaphene in the Great Lakes. Science of the Total Environment. 409:792–799.

Xia, X., Crimmins, B.S., Hopke, P.K., Pagano, J.J., Milligan, M.S., Holsen, T.M. **2009**. Toxaphene analysis in Great Lakes fish: A comparison of GC/MS techniques. *Analytical and Bioanalytical Chemistry*, 395, 457-463.

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  - Michael Milligan, Principal Investigator ,SUNY Fredonia
  - Dr. Xiaoyan Xia, Research Scientist, Clarkson University
  - Mark Omara, Ph.D. Candidate, Clarkson University
  - Tiffany Zananski, Laboratory Technician, Clarkson University

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